

8. SELENIUM

8. SELENIUM	8-1
8.1 SUMMARY	8-1
8.2 PROBLEM STATEMENT	8-1
8.2.1 Current Regulatory Status	8-2
8.2.2 Data Gaps	8-3
8.3 OBJECTIVE	8-3
8.4 PROBLEM DESCRIPTION	8-4
8.4.1 Sources	8-4
8.4.2 Biological Effects of Selenium	8-4
8.4.3 Selenium Risk Guidelines	8-6
8.4.4 Selenium Levels in the Bay-Delta	8-7
8.5 APPROACH TO SOLUTION	8-8
8.5.1 Agricultural Sources	8-8
8.5.2 Refineries	8-16

79

Se
SELENIUM

34

8. SELENIUM

8.1 SUMMARY

Selenium is a semi-metallic trace element that is widely distributed in the earth's crust at levels less than 1 milligram per kilogram (mg/kg) and with chemical properties similar to sulfur. Selenium is naturally abundant in the marine shale sedimentary rocks and soils weathered from the rocks of the Coast Ranges west of the San Joaquin Valley. The natural source of selenium in the San Joaquin Valley is erosion of the mountain soils, followed by deposition of sediment in the valley, forming the parent material for valley soils. Accelerated mobilization and transport of selenium into valley aquatic ecosystems occurs when the selenium-bearing geologic formations and soils are subjected to large flood events or disturbed by land uses such as road building, over-grazing, mining, and irrigated agriculture.

Selenium can be highly toxic to aquatic life at relatively low concentrations but is also an essential trace nutrient for many aquatic and terrestrial species. Selenium can exist in several different oxidation states in water, each with varying toxicities, and can undergo biotransformations between inorganic and organic forms. The biotransformation of selenium can significantly alter its bioavailability and toxicity to aquatic organisms. Selenium also has been shown to bioaccumulate in aquatic food webs, which highlights dietary exposures to selenium as a significant exposure pathway for aquatic organisms.

8.2 PROBLEM STATEMENT

Irrigation water applied to agricultural lands in the Grassland area of the west side San Joaquin Valley leaches selenium from the soil to the shallow groundwater table. Tile drains have been installed on some farm acreage in order to reduce the harmful effect of shallow groundwater and salt reaching the crop root zone. These drains have resulted in unintentional acceleration of selenium leaching and discharge of selenium-laden drain water into drainage ditches and the surface waters of the San Joaquin Valley. Consequently, portions of the San Joaquin River and its tributary, Mud Slough, contain elevated levels of selenium. Waterborne selenium concentrations in affected channels and sloughs frequently exceed levels considered safe for fish and wildlife species. In addition to selenium, agricultural drainage waters also contain elevated levels of boron and salts (refer to discussion under Section 7, "Salinity").

79
Se
SELENIUM
34

8.2.1 *Current Regulatory Status*

The EPA listed San Pablo Bay, Carquinez Strait, and Suisun Marsh as impaired water bodies in 1990 due to elevated selenium levels in diving ducks, which had triggered health advisories. The SFBRWQCB amended discharge permits for each of the oil refineries with the highest selenium loading to include an effluent limit of 50 ppb (daily maximum) and a mass-based limit (in pounds per day) related to the average annual flow rate and the 50-ppb concentration limit. The aquatic life criteria at that time was 71 ppb. In 1992, the EPA established an aquatic life criteria of 5 ppb for the entire Bay-Delta estuary because the salt water criteria appeared to be underprotective, as evidenced by the high potential for selenium bioaccumulation and increasing levels of selenium in Bay organisms.

The EPA listed San Pablo Bay, Carquinez Strait, and Suisun Marsh as impaired water bodies in 1990 due to elevated selenium levels in diving ducks, which had triggered health advisories.

The National Toxics Rule established the more protective fresh-water effluent limitations for the estuary for similar reasons. Several Petitions for Review were filed by various parties that ultimately were dismissed by the SWRCB because the SFBRWQCB was to address the issues. Cease and Desist Orders related to selenium discharges were issued to three refineries, requiring implementation of full-scale treatment systems or control or removal strategies by 1998. All three refineries—Tosco, Shell, and Exxon—started full-scale treatment facilities and are currently in compliance.

The SFBRWQCB determined that treatment technologies would provide the greatest emission reduction and the fastest and most economical methods to achieve selenium reduction, compared to conversion to a cleaner crude oil. Bench-scale and pilot-scale testing has occurred throughout the 1990s, and more detailed evaluations and implementation of the most promising technologies continue. Control strategies include waste stream treatment (ion exchange, biochemical treatment, and iron co-precipitation), sour water reuse, the use of an alternative crude oil, and wetland discharge. Additional environmental studies (impacts on resources, selenium/mercury interactions, immunosuppression, site-specific bioconcentration factors, and seleno-amino acids) are needed to guide resource agencies, regulators, and dischargers on improving current regulatory goals and source control actions.

The CVRWQCB has set water quality objectives for selenium and an implementation timetable for the San Joaquin River to protect beneficial uses. These objectives are most difficult to meet in the San Joaquin River just downstream of where Mud Slough discharges. In certain months, these water quality objectives have been exceeded. Further downstream, east side tributaries provide dilution water, which tends to lower the concentrations.

8.2.2 Data Gaps

No two refineries use the same processing methods or similar amounts of San Joaquin Valley crude oil in their facilities. Thus, identifying and implementing the best treatment technologies for each waste stream in each refinery have been difficult. Continued work is needed to improve the current treatment technologies and to develop new ones.

Tissue monitoring has documented selenium in bivalves (such as clams), fish, and waterfowl at concentrations known to cause impacts in similar species; but no studies have fully documented the extent of impacts that may be occurring. Additional study is needed to guide resource agencies, regulators, and dischargers on fine tuning current or proposed regulatory goals and source control actions. Data gaps include:

- Selenium bioconcentration factors from water to low trophic-level organisms (algae).
- Impacts of selenium on the reproduction of fish and waterfowl in the Bay-Delta area.
- Impacts of selenium and mercury interactions.
- Other chronic impacts on fish and wildlife, such as immunosuppression and sensory damage.
- Bioaccumulation rates and impacts of selenium in an estuarine environment versus a fresh-water environment.
- Evaluation of various seleno-amino-acids in biota to establish the toxic and ecotoxic mechanisms of selenium, critical to the establishment of site-specific water quality criteria.

Additional study is needed to guide resource agencies, regulators, and dischargers on fine tuning current or proposed regulatory goals and source control actions.

8.3 OBJECTIVE

The objective is to reduce the impairment of environmental beneficial uses in the Delta Region and in the lower San Joaquin River that is associated with selenium concentrations and loadings.

8.4 PROBLEM DESCRIPTION

8.4.1 Sources

Selenium in the lower San Joaquin River and Bay and Delta Regions originates primarily from two sources: sub-surface agricultural drainage discharged from the Grassland area on the west side of the San Joaquin Valley through Mud Slough, and waste streams from oil refineries in the Suisun Bay and Carquinez Strait area. The selenium is a byproduct of the crude oil refining process. San Joaquin Valley crude oil, used primarily by Bay Area refineries, has from 2 to 12 times higher levels of selenium compared to crude oil from other sources. Substantial amounts of selenium also are conveyed to the San Joaquin River in natural storm runoff in years with high rainfall, primarily by Panoche and Silver Creeks.

Selenium in the lower San Joaquin River and Bay and Delta Regions originates primarily from two sources: sub-surface agricultural drainage discharged from the Grassland area on the west side of the San Joaquin Valley through Mud Slough, and waste streams from oil refineries in the Suisun Bay and Carquinez Strait area.

Annual selenium loads in the San Joaquin River near Vernalis between 1986 and 1995 averaged 4,040 kg (8,906 pounds), with a range of 1,615–7,819 kg (3,558–17,238 pounds). The maximum load was in 1995, while the lowest load was in 1992. In 1991, the average riverine selenium loads that reached the estuary were approximately 2 kg/day (730 kg), while refinery loads averaged 7.1 kg/day (2,592 kg), and municipal loads averaged 2.2 kg/day (803 kg). The estimated loads from municipal sources are based on limited data; concentrations of selenium in these discharges have met the 5- $\mu\text{g/l}$ criteria. The riverine load infrequently reaches the estuary, as flows are generally insufficient and south Delta diversions draw most of the San Joaquin River water throughout the year. Only during heavy spring runoff does a significant portion of this load reach the central Delta and North Bay areas. Consequently, the selenium loads from oil refinery and municipal treatment plant activities result in the most significant impacts on the North Bay area, particularly during low riverine flow periods. From 1989 to 1992, the average annual selenium load from refineries was 2,162 kg (4,766 pounds).

8.4.2 Biological Effects of Selenium

Although selenium is an essential nutrient, levels of safe dietary uptake are narrowly bounded on both sides by adverse-effects thresholds, thus distinguishing selenium from other nutrients. Excessive levels of selenium in the diet result in reproductive impairment, poor body condition, and immune system dysfunction; similar problems are seen in low-selenium diets. Adequate human dietary levels (from food) is generally 0.1–0.3 in micrograms per gram ($\mu\text{g/g}$), but the toxicity

Excessive levels of selenium in the diet result in reproductive impairment, poor body condition, and immune system dysfunction; similar problems are seen in low-selenium diets.

threshold for sensitive animals is only 10 times higher at around 2 $\mu\text{g/g}$. Data suggest regulatory standards for selenium should be placed no more than 10 times higher than normal background levels for an adequate margin-of-safety (unless species-specific or site-specific data justify a variance from the general rule).

In fresh-water ecosystems, normal background levels of selenium in water range from 0.1 to 0.4 $\mu\text{g/l}$. Estuarine and marine ecosystems contain selenium levels in water ranging from 0.009 to 6.0 $\mu\text{g/l}$, but most levels are less than 1.0 $\mu\text{g/l}$. Sediment background levels are below 1.0 $\mu\text{g/g}$, while levels in aquatic plants are generally below 1.5 $\mu\text{g/g}$. Normal selenium levels in fish and invertebrates (whole body) are usually less than 2.0 $\mu\text{g/g}$ but have been reported as high as 4.0 $\mu\text{g/g}$. Whole-body levels in reptiles, amphibians, and birds are also less than 2.0 $\mu\text{g/g}$. In mammals, tissue levels of selenium typically average less than 2 $\mu\text{g/g}$.

Selenium occurs in natural waters primarily in two forms, selenate and selenite. Wastewater related to fossil fuel and similar sources contains mostly selenite. Drainwater from irrigated agriculture contains mostly selenate. Based on traditional bioassay measures of toxicity (24- to 96-hour exposure of an aquatic organism to contaminated water without selenium in the diet), selenite is more toxic than selenate to most aquatic organisms. Also, selenite is more readily accumulated by biota into the food chain than selenate. Direct contact with selenium in the water has only a minor effect on aquatic organisms. Adverse effects levels for selenate and selenite are generally above 1,000 $\mu\text{g/l}$. Sulfate in the water can lessen the effects of short-term exposure to high levels of selenate in agricultural drainwater but does not appear to effect the overall bioaccumulation potential of low levels of selenium.

Selenium occurs in natural waters primarily in two forms, selenate and selenite. Wastewater related to fossil fuel and similar sources contains mostly selenite. Drainwater from irrigated agriculture contains mostly selenate.

As little as 0.1 $\mu\text{g/l}$ of selenomethionine, an organic form of selenium, can accumulate in zooplankton to an average level of 14.9 $\mu\text{g/g}$ total selenium. This level of selenium in zooplankton, if fed to most species of fish, would cause dietary toxicity. Only 3.2 $\mu\text{g/g}$ selenium in the diet was sufficient to adversely affect early life stages of chinook salmon under controlled conditions. Salmonids are very sensitive to selenium pollution. Survival of juvenile rainbow trout (*Oncorhynchus mykiss*) was reduced when whole-body levels of selenium exceeded 5 $\mu\text{g/g}$. Smoltification and sea water migration among juvenile chinook salmon (*Oncorhynchus tshawytscha*) were impaired when whole-body tissue levels reached about 20 $\mu\text{g/g}$. Mortality among larvae, a more sensitive life stage, occurred when levels exceeded 5 $\mu\text{g/g}$. Bluegill embryos resulting from ovaries containing 38.6 $\mu\text{g/g}$ selenium exhibited 65% mortality.

The interactive effects of winter stress syndrome and selenium on fish are important even for waters containing less than 5 $\mu\text{g/l}$ selenium. These effects should be a critical part of selenium hazard assessments. The effects of other forms of stress (such as cold weather, migration, smoltification, disease, and

parasites) could be increased due to dietary exposure to selenium. More than 60 years ago, it was noted that chickens exposed to elevated levels of dietary selenium were susceptible to diseases. More recently, this susceptibility was confirmed for mallard ducks. Numerous other studies have confirmed selenium-induced immune system problems in wildlife.

Numerous studies have confirmed selenium-induced immune system problems in wildlife.

A very strong effect between the combination of dietary selenium and mercury in mallard hens has been reported. Selenium protected the adults from the effects of mercury, but the mercury increased the effects of selenium on the embryos in eggs laid by the adults. Selenium and mercury together in the diet of the adult hens led to significantly enhanced rates of embryo deformities (73.4% versus 36.2%) and embryo death (98.6% versus 76%). Elevated mercury levels in the North Bay and Delta due to historical mining activities and other discharges may increase the risks of selenium exposure.

8.4.3 *Selenium Risk Guidelines*

Attempts to manage risk by assessing concentrations of selenium in water is troublesome. Measurements of water-column concentrations of selenium are imperfect, and measures of total selenium loading and food web bioaccumulation are uncertain. For example, a low level of waterborne selenium can be measured either because total loading into the system is low (a low potential for hazard to fish and wildlife) or because rapid biotic uptake or sediment deposition from elevated loading has occurred (a high potential for hazard to fish and wildlife).

Water levels of selenium are useful guides for risk management only to the extent that they protect aquatic food chains from excessive bioaccumulation of selenium. The current EPA chronic criteria for selenium is 5 $\mu\text{g/l}$. Site-specific criteria for water delivery channels in the Grassland area of the San Joaquin Valley is 2 $\mu\text{g/l}$ to protect wetland uses. Numerous peer-reviewed papers, using different evaluation methods, recommend that to protect aquatic and semi-aquatic organisms, water concentrations of selenium should be from around 0.9 to 2.0 $\mu\text{g/l}$. A summary of field data shows that fish and wildlife toxicity commonly occurs in nature at waterborne selenium levels below 5 $\mu\text{g/l}$, supporting recommendations from researchers. Selenium bioaccumulates rapidly in aquatic organisms. A single pulse of selenium ($\geq 10 \mu\text{g/l}$) into aquatic ecosystems could have lasting ramifications, including elevated selenium levels in aquatic food webs.

Water levels of selenium are useful guides for risk management only to the extent that they protect aquatic food chains from excessive bioaccumulation of selenium.

Toxicity to fish and wildlife ultimately is determined by how much selenium moves into the food web. Therefore, tissue levels of selenium are more useful in developing risk guidelines. Based on a review of more than 100 papers, the

A single pulse of selenium ($>10 \mu\text{g/l}$) into aquatic ecosystems could have lasting ramifications, including elevated selenium levels in aquatic food webs.

following toxic effects thresholds for the overall health and reproductive vigor of fresh-water and anadromous fish exposed to elevated levels of selenium was recommended by one researcher: whole body (4 $\mu\text{g/g}$), skinless fillets (8 $\mu\text{g/g}$), liver (12 $\mu\text{g/g}$), and ovary and eggs (10 $\mu\text{g/g}$). This individual also recommended 3 $\mu\text{g/g}$ as the toxic threshold for selenium in aquatic food web organisms consumed by fish. Ecological risk guidelines were developed in 1993 to evaluate monitoring results from the Grassland Bypass Project in the San Joaquin Valley. These guidelines include: bird eggs (3 $\mu\text{g/g}$), whole-body fish (4 $\mu\text{g/g}$), vegetation as diet (2 $\mu\text{g/g}$), invertebrates as a food (3 $\mu\text{g/g}$), sediment (2 $\mu\text{g/g}$), and water (2 $\mu\text{g/l}$). Another researcher summarized selenium effect levels from hundreds of reviewed papers and identified similar risk thresholds.

The SFBRWQCB used ecological assessment guidelines to determine selenium loading reductions needed for the Mass Emissions Reduction Strategy for Selenium. These include total suspended material (0.45 μg organic selenium per gram [Se/g]), algae and other aquatic plants (0.45 μg organic Se/g), sediment (1.5 $\mu\text{g/g}$, dry weight), bivalves (3.2 $\mu\text{g/g}$ as elevated and 4.5 $\mu\text{g/g}$ as an alert level), and rallid (of the family *Rallidae*) eggs (2.9 $\mu\text{g/g}$ as elevated).

8.4.4 Selenium Levels in the Bay-Delta

Waterborne levels of selenium in the Bay-Delta estuary are currently less than 1 $\mu\text{g/l}$ and have been measured no higher than 2.7 $\mu\text{g/l}$ in the estuary. Although these levels are relatively low, selenium has bioaccumulated to adverse levels in biota leading SFBRWQCB staff to recommend decreasing current selenium loading to the estuary by 50% or more.

Bivalve tissue from several monitoring programs in the late 1980s and early 1990s shows elevated selenium levels in the North Bay area, ranging from 0.6 to 7.3 $\mu\text{g/g}$. Recent monitoring of the now predominant, non-native bivalve *Potamocorbula amurensis* shows that selenium levels in bivalve tissues have tripled, ranging from 10 to 18.9 $\mu\text{g/g}$ in 1995 and 1996.

In 1990, studies found up to 3.3 $\mu\text{g/g}$ whole-body selenium in juvenile striped bass from three sites in the Bay-Delta estuary. This value is just below the recommended 4- $\mu\text{g/g}$ toxicity threshold, even though waterborne selenium typically averages less than 1 $\mu\text{g/l}$ in the estuary. Striped bass collected from Mud Slough in 1986, when the annual median selenium level in water was 8 $\mu\text{g/l}$, averaged 6.9 $\mu\text{g/g}$ for whole-body selenium and contained up to 7.9 $\mu\text{g/g}$.

White sturgeon remain nearly year-round in the San Pablo Bay area, the part of the Bay-Delta estuary with some of the highest selenium levels. A 1991 report documented that developing ovaries of white sturgeon from the Bay contained as

Although waterborne levels are relatively low, selenium has bioaccumulated to adverse levels in biota, leading SFBRWQCB staff to recommend decreasing current selenium loading to the estuary by 50% or more.

much as 71.8 $\mu\text{g/g}$ selenium, or seven times over the recommended threshold for reproductive toxicity of 10 $\mu\text{g/g}$. It is highly probable that these fish are severely reproductively impaired due to selenium exposure, based on everything known regarding toxicity response functions for avian and fish eggs.

Selenium levels in clapper rail eggs have been reported as high as 7.3 $\mu\text{g/g}$. Human health advisories have been implemented due to elevated selenium levels in waterfowl from the North Bay area. Selenium levels in livers of North Bay waterfowl (scaup and scoter) are in a range (14–209 $\mu\text{g/g}$) similar to waterfowl found at Kesterson National Wildlife Refuge.

Human health advisories have been implemented due to elevated selenium levels in waterfowl from the North Bay area.

8.5 APPROACH TO SOLUTION

8.5.1 Agricultural Sources

Priority Actions

The following approaches have been identified to potentially reduce the impact of selenium discharged into agricultural drainage waters on the beneficial uses of waters.

- Drainage treatment
- Phytoremediation
- Selenium marketing
- Active land management
- Upper watershed management
- Tradable loads
- Land retirement
- Source control and drainage reduction
- Timing of release
- Drainage reuse
- Long-term solution to salinity
- Integrated on-farm drainage management and salt separation

The last five bulleted items have been discussed in Section 7, “Salinity.” The remaining items are discussed below.

Drainage treatment, phytoremediation, agroforestry, and evaporation systems activities supported by CALFED must be wildlife safe. Thus, appropriate system design and biological monitoring is necessary during pilot and implementation phases.

Drainage treatment, phytoremediation, agroforestry, and evaporation systems activities supported by CALFED must be wildlife safe.

Drainage Treatment

Drainage treatment is the removal of selenium from agricultural drainage water through processes that include ion exchange, reverse osmosis, reduction with zero-valent iron, reduction with ferrous hydroxide, reduction with bacteria and other algal-bacterial treatments, phytoremediation in agricultural drainage reuse systems, volatilization from evaporation ponds and drainage reuse systems, and flow-through wetlands.

CALFED should continue to encourage and solicit proposals for funding drainage treatment pilot projects that show potential for efficient removal of selenium from agricultural drainage water. Concurrently, CALFED could encourage and solicit proposals for marketing studies to investigate the potential for marketing selenium separated from treated drainage.

Phytoremediation

Selenium may be removed from agricultural soils by phytoremediation with selenium-accumulating crop species, either by harvesting and removal of plant material or by volatilization of selenium during the growing season.

CALFED should encourage and solicit proposals for trial demonstration projects and full-scale projects for selenium phytoremediation through uptake and volatilization by selenium-accumulating plant species with either an established or potential marketability. These trial demonstration projects would be integrated with drainage reuse through the recycling of subsurface drainage and blending with surface water irrigation supplies, in order to maximize phytoremediation, reduce selenium in discharged drainage, and reduce the recycling of selenium leached through the soil back into shallow groundwater for future discharge.

Further, CALFED should encourage and solicit proposals for the construction of small pilot evaporation systems in the Grassland area to test bioremediation of selenium and production and harvest of brine shrimp. The small evaporation systems ideally would be integrated into a drainage reuse system. CALFED could support the existing research at the Lost Hills Drainage District by funding a monitoring program.

Selenium Marketing

The goals of selenium management are to develop on-farm production of selenium utilization products from the San Joaquin Valley and to develop marketing opportunities. Selenium products include forage and nutritional supplements for animal use, vegetable and grain food products and nutritional

CALFED should continue to encourage and solicit proposals for funding drainage treatment pilot projects that show potential for efficient removal of selenium from agricultural drainage water.
